

1ST AND 2ND ORDERS																										3RD AND 4TH ORDERS																									
PROCESSES AND PROPERTIES INDEX																																																			
<div style="display: flex; justify-content: space-between;"> CA 10 </div> <p>Sulfonation reaction. XI. Preparation of monosulfonic acid by sulfonation of benzene with oleum. A. A. Spyskov. <i>Zhur. Obshch. Khim.</i> (J. Gen. Chem.) 18, 1350-5 (1948), (J. C. I. 43, 1368). -A general review of sulfonation of C_6H_6 is presented (16 references) and a procedure is described in which the deficiencies of other methods are absent. The method is based on the previous elucidation of monosulfonation mechanism (S., C. I. 33, 5820) in which interaction of C_6H_6 with H_2SO_4, in which it is insoluble results in formation of sulfonic acid which is mutually sol. in C_6H_6 and in H_2SO_4, thus carrying small amts. of C_6H_6 into soln.; the process is favored by the fact that the soly. of C_6H_6 in the sulfonic acid is reduced by water. Pure C_6H_6 was mixed with oleum in the cold, and the tube sealed and heated with agitation in a thermostat at 162-3° 9 hrs.; the oleum used was 23-7%; the resulting mixt. contained 3-4% H_2SO_4, up to 1% sulfone, and was free of disulfonic acids. Using 1.12-1.52 moles benzene in 3 hrs. at 155°, 1 mole of 27% oleum gave 76.7-82.5% monosulfonic acid, 19.1-21.5% residual C_6H_6, 7.1-7.6% H_2SO_4, 0.5-0.6% sulfone, and 5.5-1.5% water. At a 1.8:1 mol. ratio, heating 1-9.5 hrs. progressively raised the monosulfonation from 49.6 to 62%, reduced the C_6H_6 from 35.8 to 29.2%, and the H_2SO_4 from 11 to 3.5%; the sulfone content was 0.3-0.6%. Finally, at 162° 27% oleum:benzene (1:1.16) in 3 hrs. gave 73% monosulfonate, 11.8% C_6H_6, 8.3% H_2SO_4, and 1.6% sulfone; use of a 1.11 mol. ratio gave 66.1, 21.7, 5, and 0.6%, resp.; 9 hrs. heating of the latter mixt. gave 72.8% monosulfonate, 17.6% C_6H_6, 3.2% H_2SO_4, and 0.8% sulfone. Use of 22% oleum 9 hrs. at 162° and 1.15:1 mol. ratio gave 78.5% monosulfonate, 9.1% C_6H_6, 4.9% H_2SO_4, and 1.1% sulfone. The spent acid reaches 38% H_2SO_4 concn.</p> <p style="text-align: right;">G. M. Kosolapoff</p>																																																			
<div style="display: flex; justify-content: space-between;"> <div> <p>ASB-SLA METALLURGICAL LITERATURE CLASSIFICATION</p> <p>220M STYB319</p> </div> <div> <p>2ND LETTER</p> <p>1ST AND 2ND ORDERS</p> </div> <div> <p>3RD AND 4TH ORDERS</p> <p>2ND LETTER</p> </div> </div>																																																			

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Isolation of 2,4- and 2,5-xyldines from technical mixtures of isomers. VI. A. A. Spryskov (Ivanov Chem. Technol. Inst.), *Zhur. Priklad. Khim.* (J. Applied Chem.) 21, 156-163 (1948); cf. *C.A.* 32, 2094¹; 33, 1289¹.—The disocn. const. of 2,4-, 3,4-, 2,5-, 2,3- and 1,6-xyldines, detd. by pH measurements of solns. of the corresponding amine-HCl are, resp., 2.8×10^{-9} , 2.2×10^{-9} , 1.4×10^{-9} , 1.3×10^{-9} , 4.1×10^{-10} . Sepn. of the isomers with a soln. of HCl in PhMe is not satisfactory, but it confirms that 2,4-xyldine is a stronger base than the 3,4- and 2,5-isomers, 2,5-xyldine stronger than the 1,6-isomer, and 3,1-xyldine stronger than the 2,5-isomer. The best method for sepg. 2,4-xyldine (IA) from a tech. mixt. with HCl in a solvent is one using $C_6H_5Cl_3$ (tech. mixt. called "polychloride") (I). Salt formation during the process was followed by detns. of sp. wts. of I soln. of xyldine (the sp. wt. plotted vs. xyldine content in % gives a straight line). The best ratio of I to xyldine is 65:35, since the salt is quite sol. in the latter and an excess of it is to be avoided. At room temp. the soly. of IA in 100 g. I is about 0.04 g. and that of HCl somewhat less than 0.4 g. In 4 expts. the meta isomers in the product ranged from 90.0 to 93.9%. The mother liquor from this separation contains about 31% isomers consisting of 75% para and ortho and 25% meta compds. 2,5-Xyldine is sepd. by dropwise addn. of $H_2SO_4 \cdot H_2O$ to the liquor with heating and stirring, removing the solvent, adding Na_2SO_4 to the hot soln. of the product, filtering the sulfate, and analyzing the filtrate by diazotization and bromination. Thus 90% pure 2,5-xyldine is obtained in 50% yield after removal of the *m*-isomer or in 25% yield from the original mixt. Kitty Luss

SERYSKOV, A. A.

Fedorev, B. P. and Seryskov, A. A., The separation of 1,5- and 1,8-dinitronaphthalene. P. 1014

SO: J. Applied Chem. (USSR) 21, No. 10 (1948)

Methods are worked out for the separation of technical dinitronaphthalene into 1,5- and 1,8-isomers by crystallization from a solution of sulfuric acid and from aniline. The solubility of 1,5- and 1,8-dinitronaphthalenes in aniline, sulfuric acid, acetone and methanol is determined at various temperatures.

The Ivanov Chemico-Technological Inst.
February 16, 1948

SPRYSKOV, A. A.

PA 64T6

USSR/Chemistry - Xylydines, Isomers of Feb 1948
Chemistry - Precipitation

"Precipitation of m-4 and p-Xylydines from Commercial Mixtures of Isomers, VI," A.A. Spryskov, Ivanovo Chem Technol Inst, 8 pp

"Zhur Prik Khim" Vol XXI, No 2

Determined dissociation constants for xylydine isomers and studies of the method of propagation of isomers by hydrogen chloride in organic solutions. Method separates m-4-xylydine by hydrogen chloride from commercial mixtures. Results in 90% pure m-4-xylydine and about 50% by amount from the original solution. Submitted 24 Jan 1947.

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Sulfonation reaction. XII. The preparation of the
chloride of 1,3-naphthalenedisulfonic acid from its sodium
salt. A. A. Spryskov and N. V. Apar'eva (Ivanov State
Med. Inst.). *J. Gen. Chem. U.S.S.R.* 19, 1589-94(1949)
(Engl. translation).—See *C.A.* 44, 10826. B. L. M.

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Sulfonation reaction. XII. Preparation of the chloride of 1,5-naphthalenedisulfonic acid from its sodium salt. A. A. Spryskov and N. V. Apar'eva. *Zhur. Obshchei Khim.* (J. Gen. Chem.) 19, 1576-82(1949); cf. *C.A.* 43, 2178c. Heating 1,5-C₁₀H₆(SO₃Na)₂ with 10 moles ClSO₃H 2 hrs. at temps. from 16° to 114° showed the max. yield of the disulfonyl chloride to occur at 98°, when yields of 93% are reached; the yield declines sharply above 100°

(46% at 114°); the product, m. 182°, is also most pure under these conditions. The yield loss is caused by incipient trisulfonation, as shown by the formation of a trisulfonyl chloride (shown by hydrolysis and Cl detn.) upon heating the reaction mixt. 10 hrs. to 114°; this product, m. 145°, appears to be almost pure 1,3,5-isomer. Study of the time factor at 10°, 65°, and 100° showed that at 10° a condition approximating equil. is reached in 200-500 hrs. at 89-91% yield; at 65° this takes place in 14 hrs., while at 100° the above mentioned max. is reached in about 2 hrs., when an 84% yield may be attained. Similarly, excess ClSO₃H (up to 10 ml./g.) at 65° gives almost 100% conversion in 6-8 hrs. The use of dry salt is imperative, as a product with 1.85% moisture gives yields lowered by 10-12%; drying must be done 2-3 hrs. at 200°. Neither NaCl nor Na₂SO₄ admixts. (up to 20%) affect the yield or quality of the product. The disulfonyl chloride is readily hydrolyzed only by boiling H₂O, and almost as rapidly by hot 5% H₂SO₄ (small samples require about 1 hr.).

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Sulfonation reaction. XIII. Hydrolysis of sulfonic acids. A. A. Spryskov and N. A. Ovsyankina (Ivanovsk. Chem.-Technol. Inst.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 20, 1043-9 (1950); cf. *C.A.* 43, 2178e. --Hydrolysis of $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ with H_2O at 100° for 4 hrs. gives a hydrolysis max. (8.5%) when 0.58 mole H_2O /mole acid is used; lower or higher proportions of H_2O give lower degrees of hydrolysis; with 47.5% H_2SO_4 this max. (12.3%) is reached at about 1.4 moles H_2O present, while in 60% H_2SO_4 the max. is at nearly 3 moles. $\text{C}_6\text{H}_5\text{SO}_3\text{H}$ with 1 mole H_2O is not hydrolyzed at 117° while in 30% HCl hydrolysis is noticeable even at 113° ; under the same conditions the 1-isomer hydrolyzes 50 times faster, although in pure H_2O no hydrolysis at 78° occurs. *p*-Sulfosalicylic acid is hydrolyzed by H_2O only above 100° , while with 30% HCl hydrolysis proceeds at a measurable rate even at $63-70^\circ$ and rather rapidly at 86° . With *p*- $\text{ClC}_6\text{H}_4\text{SO}_3\text{H}$ only a slight hydrolysis occurs at 100° in 30% HCl (none in H_2O) and at higher temps. (up to 140°) the rates are very close; 60% H_2SO_4 gives similar results. Hence the min. temp. of hydrolysis of a sulfonic acid is not a const. but varies depending on the conditions and medium used. The results are given graphically.

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Sulfonation reaction. XIV. Preparation of sulfonyl chlorides from sodium sulfonates. A. A. Spryskov and N. V. Apar'teva (Ivanovsk Chem. Technol. Inst.), *Zhurnal Khim. (J. Gen. Chem.)* 20, 1818-25 (1950); cf. C.I. 44, 10821, 9367h. Use of ClSO_3H permits the prepn. of sulfonyl chlorides in high yield from the Na sulfonates of aromatic compds. contg. Me, CO-H, OH, NO_2 , or SO_3H groups. Generally the ease of prepn. parallels the ease of sulfonation of the respective nuclei. Heating 4 ml. ClSO_3H with 2 g. PhSO_3Na 2 hrs. at $85-100^\circ$ (85° is preferable) yields 96.5% PhSO_2Cl , m. 12-13.5° (a higher temp. gives a product m. 11°), isolated by pouring on ice and drying *in vacuo*; crystn. from petr. ether gives the pure substance, m. 16.3° . *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{Na}$ is best prepd. at 16° , 92-4°, of a product m. 64-65° being obtained in 2 hrs.; at 0° the product is purer and m. 68° . *p*- $\text{MeC}_6\text{H}_4\text{SO}_3\text{K}$ gives 97.5% chloride, m. 33-5°, after 2 hrs. at 100° or 20 hrs. at 15° ; Na sulfosalicylate added to ClSO_3H at $5-7^\circ$ gives the chloride, m. 17.2° , in 71° yield after 24 hrs. at 11° ; 1 hr. at 63° gives 81% of a product, m. 16.7° , while 89% of a product m. 165° is obtained from 20 ml. ClSO_3H with 4 g. Na salt. 1- and 2- $\text{C}_6\text{H}_5\text{SO}_2\text{Cl}$, m. 98-113°, form even at -10° from 2- $\text{C}_6\text{H}_5\text{SO}_3\text{Na}$, although the 1-isomer, m. 66° , is formed in 40% yield after 2 hrs. at $12-15^\circ$. *m*- $\text{O}_2\text{NC}_6\text{H}_4\text{SO}_2\text{Cl}$, m. 63° , forms in 93% yield after 2 hrs. at 85° or in 67% yield in 68 hrs. at 15° . Similarly, *m*- $\text{C}_6\text{H}_4(\text{SO}_2\text{Cl})_2$, m. 60° , forms from the di-Na salt, best either in 2 hrs. at 130° (57.3%) or in 6 hrs. at 65° (40.2%); lower temps. give a less pure product, unless the reaction is run longer; the highest yield (63.8%) is obtained in 2 hrs. at 85° . 1,3,5-Naphthalenesulfonoyl chloride, m. $144-5^\circ$, forms best (80%) after 2 hrs. at 140° . All the salts are carefully dried before use and freshly distd. ClSO_3H is used. G. M. K.

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Sulfonation reaction. XV. Some properties of mono-sulfonated naphthalenes. A. A. Spryskov (Ivanovsk Chem.-Technol. Inst.). *Zhur. Obshch. Khim.* (J. Gen. Chem.) 20, 2101-4 (1950); cf. *C.A.* 42, 8944; 45, 2434a.—
 $1\text{-C}_{10}\text{H}_7\text{SO}_3\text{H}$ dried in air contains somewhat over 2 H_2O ; 1 H_2O is readily lost by drying over solid KOH or NaOH or

P_2O_5 ; the latter at 45-55° (80 hrs.) gives the anhyd. product; in *vacuo* the drying may be complete in 4-6 hrs. at 55°; the product m. 139-40°. The 2-isomer forms a trihydrate, m. 83°; drying over CaCl_2 gives a monohydrate, m. 124°, which also forms on drying over KOH, NaOH, or P_2O_5 at room temp.; P_2O_5 at 77° gives the anhyd. acid, m. 90.5-1.0°. The soly. of the 1-isomer in 20% HCl at 0° is 2.23 g./100 g. soln.; that of the 2-isomer is 0.22. $1\text{-C}_{10}\text{H}_7\text{SO}_3\text{Na}$ forms a monohydrate giving the anhyd. salt at 130°; its soly. in H_2O is 8 g./100 g. at 0°, 12.9 at 28°, 31.8 at 80°, 38.9 at 96°; at 0° its soly. in 24% NaCl is 0.04 g./100 g.; in 20% NaCl 0.07; in 15% NaCl 0.33, while at 26° its soly. in 15% NaCl is 0.47 and at 30° its soly. in 26% NaCl is 0.13 g./100 g. The soly. of $2\text{-C}_{10}\text{H}_7\text{SO}_3\text{Na}$ in H_2O is 3.2 g. at 0°, 4.1 g. at 10°, 13.1 g. at 60°, 19.6 at 86°, 22.5 g. at 96°; it is almost completely salted out at 25-65° by concd. solns. of NaCl and Na_2SO_4 , while the 1-isomer is salted out only partially at 69°. G. M. Kosolapoff

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Sulfonation reaction. XV. Some properties of mono-sulfonated naphthalenes. A. A. Spryskov, *J. Gen. Chem. U.S.S.R.* 20, 2177-W(1950) (Engl. translation).—See *C.A.* 45, 5669d. B. L. M.

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Sulfonation reaction. XVI. Equilibrium between a sulfonic acid and its chloride. A. A. Spryskov and Yu. L. Kuz'mina (Ivanovsk. Chem. Technol. Inst.), *Zhur. Obshch. Khim.* (J. Gen. Chem.) 21, 714 (1951); cf. C. 1 45, 5239. Allowing mixts. of *p*-MeC₆H₄SO₃Cl (I) with the sulfonic acid (II) and H₂SO₄ to stand at 0° for 0.5-32 hrs. showed that the I in such mixts. is gradually transformed until an equil. is reached between I and II, the position of which depends on the relative amt. of II and H₂SO₄. At 0° the equil. const. is 1.18. The equil. state is reached in 4-9 hrs.
G. M. Kosolapoff

Sulfonation reactions. XVII. Hydrolysis of sulfonic acids in the presence of hydrochloric, sulfuric, and phosphoric acids. A. A. Spryskov and N. A. Osvyankina (Ivanovsk State Med. Inst.), *Zhur. Obshchei Khim.* (U.S.S.R. Gen. Chem.) 21, 1508 (1951); cf. C.A. 44, 8367h, 45, 8993i. — Hydrolysis of 1-C₆H₅SO₃H (I) and 3-sulfosalicylic acid (II) is accelerated by mineral acids in a different way. HCl gives the greatest acceleration, H₃PO₄ is least effective while H₂SO₄ is intermediate. H₃PO₄ of 90% concn. almost has no effect on hydrolysis of II. II, prepd. by heating salicylic acid 0 hrs. with 95% H₂SO₄ in 210.5–21.0° (anhyd.). The hydrolyses were run by heating 0.5–1.0 g. samples of the acids in sealed tubes with known amts. of H₂O and mineral acid, and following the reaction by SO₂ detns. The results, given graphically, indicate the following concns. of the various mineral acids that give the indicated hydrolysis extent. With I, 4% hydrolysis by 6% HCl, 14% H₂SO₄, 25% H₃PO₄; 25% hydrolysis by 24.5, 47, and 76% acids, resp.; 35% hydrolysis by 27, 52, and 80% acids, resp. With II, 10% hydrolysis by 6.5% HCl, 26% H₂SO₄, and 80% H₃PO₄; 20% hydrolysis by 17% HCl or 41% H₂SO₄ (H₃PO₄ is mentioned only in the example above), and 35% hydrolysis by 27% HCl or 50% H₂SO₄. In all expts. the hydrolysis was run 25 hrs. at 100° in the presence of total of 4.5 moles H₂O, but with varying amts. of mineral acids to give the requisite concn. G. M. Kosolapoff

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Sulfonation reaction. XVII. Hydrolysis of sulfonic acids in the presence of hydrochloric, sulfuric, and phosphoric acids. A. A. Spitskov and N. A. Ovsyankina. *J. Gen. Chem. USSR*, 21, 1610-52 (1951) (Engl. translation) *Sov. Chem.* 40, 252-61. R. R.

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Sulfonation reaction. XVIII. Equilibrium between 2,5-dichlorobenzene-sulfonic acid and its sulfonyl chloride. A. A. Spryskov and Yu. L. Kuz'mina (Ivanovsk Chem.-Technol.). *Zhur. Obshchei Khim.* (J. Gen. Chem.) 21, 1887-91 (1951); cf. *C.A.* 45, 8963d; 46, 2523d.—Keeping mixts. of 2,5-Cl₂C₆H₃SO₂Cl with H₂SO₄ and ClSO₃H at 0° up to 150 hrs. gave an equil. const. between the acid and the chloride of 0.63 (av. value), even with a wide variation of the components. The results agree with those calcd. from theoretical considerations to within 1-2%. The equil. const. at 80°, measured similarly, was 0.67. Generally, equil. is reached within 1 hr. at 80°. The heat effect of the transformation of this sulfonyl chloride to the free acid is therefore nearly zero. The starting sulfonyl chloride m. 36.5° (crude), m. 37.5-8.0° (from Et₂O). XIX. Preparation of 1,3,5-naphthalenesulfonyl chloride. A. A. Spryskov. *Ibid.* 2022-7; cf. *C.A.* 42, 804h.—Reaction of pure 1,5-C₁₀H₆(SO₂Cl)₂, m. 183-4°, with ClSO₃H (b.p. 70-80°) even at 77-8° proceeds rapidly and with excess ClSO₃H (50 moles) can be completed in 6 hrs., yielding pure 1,3,5-naphthalenesulfonyl chloride, m. 146°. At 146-9° the reaction is complete in 0.5 hr., even with only 2 moles excess of ClSO₃H. The best yields (84-85%) are obtained at lower temps. (78-100°) with a large excess of ClSO₃H. The ClSO₃H should be distd. carefully before use for the best yields and a pure product; a repeatedly distd. product gives up to 97% of the trisulfonyl chloride. During the distn. some SO₂Cl₂ and possibly pyrosulfonyl chloride form. Addn. of P₂O₅ (about 1 mole) to ClSO₃H improves the yield. G. M. K.

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Sulfonation reaction. XX. Sulfonation of sulfonic acids, their sodium salts, and sulfonyl chlorides. A. A. Spryskov and A. I. Kobenin (Ivanovsk Chem. Tech. Inst.), *Zh. Obshchei Khim.* (J. Gen. Chem.) **72**, 201-4 (1962); cf. C.A. **46**, 8604c, 8653g, 10099d; 10123k; preceding abstr.—Sulfonation of $2\text{-C}_6\text{H}_4\text{SO}_2\text{Cl}$ is much more rapid than that of the free acid, which, in turn, is more rapid than that of the Na salt. $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{H}$ derivs. display the same order of reactivity. The sulfonyl chloride sulfonates more rapidly because of the consumption of 1 mole H_2O in its hydrolysis. Sulfonation with ClSO_3H is also retarded by the presence of Na sulfonates. G. M. Kosolapoff

Spryskov, A.A.

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Mar. 10, 1954
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Sulfonation reaction. XXII. Preparation of naphtha-
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Chem. Technol.). *J. Gen. Chem. U.S.S.R.* 22, 727-31
(1952) (Engl. translation).—See *C.A.* 47, 8709g.

H. L. H.

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SPRYSKOV, A.A.; APAR'YEVA, N.V.

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derivatives of naphtholdisulfonic acids. Zhur. Obshchay Khim. 22,
1624-31 '52. (MLRA 5:9)
(CA 47 no.17:8710 '53)

Spryskov, A. A.

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(3)³
Sulfonation reaction. XXI. Determination of some di-
sulfonic acids of naphthalene. A. A. Spryskov and B. I.
Karnyayev. *J. Gen. Chem. (U.S.S.R.)* 22, 1003-6 (1952)
(Engl. translation).—See C.A. 47, 8700c. XXIII. Prep-
aration of chlorides and other derivatives of the naphthol-
disulfonic acids. A. A. Spryskov and N. V. Apar'eva.
Ibid. 1907-73.—See C.A. 47, 8710b. XXIV. Hydrolysis
of naphthalenedisulfonic acid. A. A. Spryskov and B. I.
Karnyayev. *Ibid.* 1911-14.—See C.A. 47, 8710i.

H. L. H. *HK*

1. SPRYSKOV, A.A. KARAY'YEV, B.I.

2. USSR (600)

4. Sulfonic Acids

7. Sulfonation. Part 24, Hydrolysis of naphthalene-disulfonic acids.
Zhur.ob.khim. 22 no. 10, 1952

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SPRYSKOV, A.A.

Sulfonation reaction. XXV. Some properties of naphthalenetrisulfonyl chlorides. Zhur. Obshchey Khim. 22, 2035-8 '52. (MLRA 5:12)
(CA 47 no.18:9314 '53)

1. Ivanovsk Chem.Technol. Inst.

SPRYSKOV, A. A.

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Determination of copper in manstrol blue. N. P. Kanyayev and A. A. Spryskov (Chem. Technol. Inst., Ivanovo). *Zhur. Priklad. Khim.* 25, 1220-1 (1952).—Tech. and purified $C_{20}H_{11}N_3Cu$ were analyzed by digestion with HNO_3 , the former yielded 10.47 and 10.31% Cu, and the latter 10.97, 11.01, 11.09, and 11.10 instead of the theoretical 11.03%. Purification consisted in dissolving the pigment in 98% H_2SO_4 , dilg. at 80–85° to 78% acid, filtering, washing with 78% H_2SO_4 , and finally with boiling H_2O . Method of analysis consisted of dissolving 1 g. of pigment in 35 ml. of concd. HNO_3 and heating until all of the HNO_3 was driven off and some phthalic acid began to come over; care must be taken to avoid ignition and any of the material creeping up along the walls is washed down with HNO_3 . The temp. was raised to red heat, the residue cooled and weighed.

I. Bencowitz

SPRYSKOV, A. A.

The determination of copper in manastrol blue. N. P.
Kanyayev and A. A. Spryskov. J. Appl. Chem. U.S.S.R.
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H. L. H.

SPRYSKOV, A. A.

The sulfonation reaction. XXVII. Equilibrium between polysulfonic acids and their chlorides. A. A. Spryskov and Yu. L. Kuz'mina (Chem. Technol. Inst. and State Med. Inst., Ivanovo). *Sbornik Statei Obshchei Khim., Akad. Nauk S.S.S.R.* 1, 559-63 (1953); cf. *C.A.* 46, 6808c; 48, 3321f. — Equil. between $m\text{-C}_6\text{H}_4(\text{ClO}_3\text{S})_2$ and $m\text{-(ClO}_3\text{S)C}_6\text{H}_4\text{SO}_3\text{H}$ in a mixt. of H_2SO_4 and ClSO_3H was studied at 80° . The equil. const. was found to be 1.33. In the equil. between $1,3,5\text{-C}_6\text{H}_3(\text{SO}_3\text{Cl})_3$ and the corresponding sulfonic acid in a mixt. of $\text{H}_2\text{SO}_4\text{-ClSO}_3\text{H}$ studied at 100° , the equil. const. was found to be 1.90. The equil. is established with the formation of $\text{SO}_3\text{H-SO}_3\text{Cl}$ derivs. and can be calcd. from the 1st order reaction equation. Equil. is attained in 3 hrs. or less. XXVIII. Preparation and properties of 1,3-naphthalenedisulfonic acid and its derivatives. A. A. Spryskov and O. S. Ivanova. *Ibid.* 564-7. — Treatment of di-Na 1,3-naphthalenedisulfonate with PCl_5 or ClSO_3H yields the corresponding dichloride; the pure di-Na salt gives 70% yield of a product which is not pure, m. $125\text{--}36^\circ$. The salt from com. amino-G-acid gave a 60% yield of dichloride when treated with SO_2Cl_2 . The $1,3\text{-C}_{10}\text{H}_6(\text{SO}_3\text{Cl})_2$ is best purified from CS_2 , which yields the pure material, m. 131° , very readily (cf. Fierz-David and Richter, *C.A.* 40, 18214). Hydrolysis in aq. EtOH at 80° and evapn. gave the free acid with $4.5\text{H}_2\text{O}$, which is very hygroscopic. In H_2O at 100° only 0.7% of the dichloride is hydrolyzed in 100 hrs. The pure di-Na salt (from the free acid) forms a very stable monohydrate (even at 200°), while air-dried material forms an adduct with 2.5 mols. H_2O . Its soly. in 24% NaCl soln. at 20° is 7.4 g. per 100 g. Mg salt octahydrate is formed from the free acid and MgCO_3 ; at 195° it becomes anhydrous; the Mg salt is sol. in H_2O and its soly. is 20.2 g. per 100 g. at 20° . Ca salt tetrahydrate loses 2.5 mols. H_2O at 130° ; its soly. in H_2O at 20° is 26 g. per 100 g. Ba salt trihydrate loses 1 H_2O at 200° ; its soly. in H_2O at 20° is 32.88 g. per 100 g. The benzidine salt is anhydrous at 100° ; in open vessel it slowly forms a trihydrate; its soly. in H_2O is 0.08 g. per 100 g. at 0° , 0.39 g. at 20° , and 6.0 g. at 99.9° . The benzylthiourea salt forms a trihydrate, m. 92.5° (from 0.1N HCl), becoming anhydrous at 100° ; its soly. in H_2O is 0.39 g. per 100 g. at 20° . G. M. Kosolapoff.

Spryskov, A.A.

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Sulfonation reaction. XXIX. Relative activity of sulfonating agents. A. A. Spryskov (Chem. Technol. Inst., Ivanovo). *Sbornik Spisokovskoy Khim.* 2, 515-51 (1953); cf. C.A. 47, 8709g; 49, 8341f. The relative activity of sulfonating agents was detd. by sulfonation of 1,3,7- and 1,3,5- $C_6H_3(SO_2Cl)_2$ at 150-70° and of 1,5- $C_6H_3(SO_2Cl)_2$ at 100°. The following descending order of activity was found: 55% oleum, 75% oleum, 80%, H_2SO_4 , H_2SO_3 . The m.p. diagram of the $C_6H_3(SO_2Cl)_2$ -1,3,5- $C_6H_3(SO_2Cl)_2$ system was detd. (% 1,5-dichloride and temp. of liquefaction at beginning and end, resp., shown): 10.1, 123°, 142°; 20, 127.5°, 137.5°; 25, 128°, 141.2°; 25.5, 128°, 133°; 30, 128°, 130°; 31.5%, 128°, 131.5°; 35, 127.5°, 133.5°; 40, 127.5°, 139.2°; 50, 128°, 140°; 60, 128°, 155.5°; 69.2, 128.5°, 167°; 80, 132°, 176°; 89.9, 130°, 180.5°. XXX. Mechanism of hydrolysis of sulfonic acids. A. A. Spryskov and N. A. Ovsyankina. *Ibid.* 382-6. The hydrolysis of p - $BrC_6H_4SO_3H$ and the p -Cl analog in 30% HCl and 55% H_2SO_4 was studied. The hydrolysis of 1- $C_6H_3SO_3H$ and sulfosalicylic acid in the presence of 0-89% AcOH was also studied. The rate of hydrolysis in the presence of mineral acids does not rise proportionally to the concn. of the latter but lags behind it.

A. A. SPRYSKOV

The rate of the observed hydrolysis is detd. by the concn. of a transitional complex, formed by addn. of H_2O^+ to the SO_3H group; this complex then reacts with the available bases (Cl^- , HSO_4^- , RSO_3^-), yielding the hydrocarbon, H_2SO_4 , and the secondary acid product; the 2nd reaction is the rate-controlling step for the hydrolysis. Presence of $AcOH$ retards hydrolysis of the sulfuric acids in comparison with hydrolysis in its absence; this is explained by reaction of the sulfonic acid with $AcOH$ as a base, yielding RSO_3^- ions and $AcOH_2^+$ ions; the RSO_3^- ions displace the equil. in the aq. system so as to hinder the aq. ionization of RSO_3H , thus reducing the concn. of effective H_2O^+ ions and thus reducing the concn. of the transitional complex. The latter is represented as a polar structure (δ -dipole). Hydrolyses (see above) with 30% HCl and 55% H_2SO_4 were very slow under 160° , at which temp. a rapid reaction commences.

G. M. Kosolapoff

SPRYSKOV, A. A. and OVSYANKINA, N. A.

Study of the Reaction of Sulfonation. XXX. On the Mechanism of Hydrolysis of Sulfonic Acids, page 882, Sbornik statey po obshchey khimii (Collection of Papers on General Chemistry), Vol II, Moscow-Leningrad, 1953, pages 1680-1686.

Ivanovo Chemico-Technological, and Ivanovo State Medical Inst

SPRYSKOV, A. A.

Chemical Abst.
Vol. 48 No. 6
Mar. 25, 1954
Organic Chemistry

Sulfonation reaction. XXVI. Determination of some di- and trisulfonic acids of naphthalene. A. A. Spryskov and B. I. Karavaev (Izvestiya Akad. Nauk SSSR Khim. Obshchest. Khim. 23, 284-7 (1963); cf. C.A. 47, 9314c. — The estn. of naphthalenedisulfonic acids which are sulfonated to either tri- or tetrasulfo derivs. is described. The limit of error is within 1%. Sulfonation with oleum of the 1,5-, 1,7-, and 2,6-isomers yields 1,3,5,7-tetrasulfonaphthalene, while the 1,6- and 2,7-isomers give the 1,3,6-trisulfo deriv. The 1,3-isomer is converted to 75% 1,3,5,7-tetrasulfo deriv. The chloride of the latter is nearly insol. in C_6H_6 while the 1,3,6-trisulfonyl chloride dissolves to the extent of 10.7 g./100 g. The following procedure was evolved. A 3-g. sample of the sulfonation mixt. contg. some 1 g. disulfonic acids is treated with 7 ml. 65% oleum, sealed in a tube, heated in an Fe pipe 2 hrs. to 161-3°, 15 ml. Cl_2O_2 added, the mixt. heated 1 hr. at 120-5°, quenched with ice, the sulfonyl chlorides (0.5-0.6 g.) are filtered off, weighed, washed with C_6H_6 (six 5 ml. portions), and the residue is again weighed. If the washings leave no residue on evapn. the washing is terminated. The content of 1,5-, 1,7-, and 2,6-disulfonic acids is calcd. by formula: $\% = 430/[5.3(a/b) - 1]$, where a is wt. of tri- and tetrachlorides, and b is the wt. of the tetrachlorides. G. M. Kosolapoff

SPRYSKOV, A.A.; KARAVAYEV, B.I.

Study of the reaction of sulfonation. Part 32. Isomerization of naphthalene disulfonic acids. *Zhur.ob.khim.* 23 no.7:1182-1188 J1 '53. (MLBA 6:7)

1. Kafedra organicheskoy khimii Ivanovskogo khimiko-tekhnologicheskogo instituta. (Naphthalene) (Sulfonic acids) (Isomerism)

SPRYSKOV, A. A.

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Sulfonation reaction. XXXIII. Equilibrium between
sulfonic acids and their chlorides. A. A. Spryskov and
Yu. L. Kuz'mina (Ivanov Chem. Technol. Inst.; also
Ivanov State Med. Inst.). Zhur. Obshchei Khim. 23,
1730-9 (1953); cf. C.A. 48, 8608c; 47, 12327a. On the
basis of the equation $\text{RSO}_2\text{Cl} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{RSO}_3\text{H} + \text{HSO}_4\text{Cl}$,
the equil. consts. were detd. at 80° for several sulfonic acids.
The const. for $p\text{-O}_2\text{NC}_6\text{H}_4\text{SO}_3\text{H}$ and its chloride is 0.51; for
 $m\text{-HO}_2\text{CC}_6\text{H}_4\text{SO}_3\text{H}$ and its chloride 1.22, and for 4,1,3-
 $\text{MeC}_6\text{H}_3(\text{SO}_3\text{H})_3$ and its chloride 0.9. G. M. Kosolapov

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SPRYSKOV, A. A.

Sulfonation reaction. XXXI. Initial ratios of naphthalenedisulfonic acids. A. A. Spryskov and B. I. Karavaev (Ivanovsk Chem. Technol. Inst.). *Zhur. Obshch. Khim.* 23, 1712-18(1953); cf. C.A. 48, 3321f. At low temp., sulfonation of $C_{10}H_8$ gives a greater yield of the more hydrolyzable isomer. Sulfonation of $C_{10}H_8$ with 99.8% H_2SO_4 10 hrs. gave 85-85.5% 1- $C_{10}H_7SO_3H$ either at 0° or at 56-7° (the yield is given as percent of the total monosulfonation products). Disulfonation did not take place. The 1-isomer was isolated by pptn. with *m*-nitro-*o*-anisidine. Vacuum-dried 1- $C_{10}H_7SO_3H$ was treated with 20.4% oleum 5 hrs. at 56-7°, the products, analyzed as to 1,5-disulfonate content by the benzidine and xyldene method, contained 75% 1,5-, 10% 1,6-, and 15% mixed 1,3- and 1,7-disulfonic acids. Sulfonation of 2- $C_{10}H_7SO_3H$ 5 hrs. at 56-7° with 99.5% H_2SO_4 gave 67% 1,6-, 21% 1,3- and 1,7-, 11% 2,7-, and 1% 2,8-disulfonic acids and 1.2-3.6% trisulfonic acid. G. M. Kosolapoff

Spryskov, A. A.

USSR/Chemistry - Sulfonation reaction

Card 1/1 Pub. 151 - 19/37

Authors : Spryskov, A. A., and Ovsyankina, N. A.

Title : Investigation of sulfonation reaction. Part 34.- Hydrolysis of sulfo-acids of the benzene series

Periodical : Zhur. ob. khim. 24/10, 1810-1814, Oct 1954

Abstract : The orientation of various substitutes in the benzene nucleus and its effect on the rate of hydrolysis of sulfo-acids, isomerization of the para-isomer of phenolsulfonic acid and hydrolysis of benzene polysulfonic acid, was investigated. It was found that the hydrolysis reaction of mono substituted sulfo-acids of the benzene series takes place at different rates depending upon the position of the substitute. The order of the kinetic stability of isomers toward hydrolysis is described. Conditions favorable for the hydrolysis of certain benzene sulfonic acids are listed. Seven references: 2-USSR; 3-USA; 1-German and 1-Czech (1884-1951). Tables.

Institution : State Medical Institute and Chemical-Technological Institute, Ivanov

Submitted : April 28, 1954

SPRYSKOV, A. A.

✓ Sulfonation reaction. XXXV. Preparation of toluenedi-
 and trisulfonates. A. A. Spryskov and T. I. Yakovleva
 (Chem. Technol. Inst., Ivanovo). *Zhur. Obshchei Khim.*
 25, 783-8; *J. Gen. Chem. U.S.S.R.* 25, 749-51 (1955) (Engl.
 translation); cf. C.A. 47, 8709g; 49, 12342d. — Heating 4 g.
 p -MeC₆H₄SO₂Cl with 11.5 ml. distd. ClSO₃H in 10 min. to
 145° and keeping the mixt. at 145-7° 0.5 hr. gave complete
 conversion to the disulfonyl chloride, m. 52.4-2.8°; longer
 heating yields a less pure product with lower m.p. The
 product obtained is pure 2,4-toluenedisulfonyl chloride, ob-
 tained in 52% yield after quenching the mixt. in H₂O. The
 residual material consists mainly of the sulfonic acids.
 The 3rd sulfo group cannot be introduced even at reflux
 with ClSO₃H. At 20° the 2,4-isomer is sol. in 100 g. Et₂O
 to the extent of 73.6 g. This dichloride (1 g.) with 1 ml.
 30-60% oleum in a sealed tube 4 hrs. at 180° yields with
 ClSO₃H 2,4,6-toluenetrisulfonyl chloride (I), m. 158-61°;
 introduction of 24 ml. ClSO₃H into a mixt. of 6 g. dichloride
 and 6 ml. 38% oleum and heating again 0.5 hr. at 145-8°
 gave 54% trichloride. The trichloride, m. 157-9°, was
 also formed on heating 2 g. p -MeC₆H₄SO₂Cl with 2 ml. 67%
 oleum 4 hrs. at 180°, followed by the above treatment with
 ClSO₃H. Pure I, m. 162° [from AcOH; cf. Klason, *Ber.*
 14, 307 (1881)] is sol. in hot AcOH, MePh, C₆H₆, CHCl₃,
 (CH₂Cl)₂, and ClSO₃H. The soly. in Et₂O at 20° is 0.73 g.
 per 100 g. soln. G. M. Kosolapoff

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✓ Sulfonation reaction. XXXVI. Sulfonating activity of
alumina. A. A. Spryskov. J. Gen. Chem. U.S.S.R. 25.
1683-5 (1954) (Engl. translation).—See C.A. 50, 5506f.
B. M. R.

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Spryskov, A.A.

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Sulfonation reaction. XXXVII. Equilibrium between
the sodium sulfonate, sulfonic acid, and its chloride. A. A.
Spryskov and N. V. Alekseyeva (Chem. Technol. Inst. Moscow
49, 100-106; 50, 6509). The equil. between $2,5\text{-Cl}_2\text{C}_6\text{H}_3$
 SO_3H , its Na salt, and its chloride in a medium of H_2SO_4
 and ClSO_3H was detd. at 40° . The equil. const. is 0.33.
 It was shown that the compn. of the equil. mixt. can be
 computed to within 1-2% of the true condition by graphical
 soln. The rate of conversion of the salt into the acid and
 the chloride increases at high proportions of ClSO_3H in the
 reaction mixt.
 G. M. Kosolapoff

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Spryskov, A.A.
USSR/ Chemistry - Reaction processes

Card 1/1 Pub. 22 - 25/49

Authors : Spryskov, A. A.

Title : Reaction of perchloric acid with sulfuric anhydride

Periodical : Dok. AN SSSR 100/5, 937-938, Feb 11, 1955

Abstract : The reaction between sulfuric anhydride and perchloric acid was investigated for the purpose of explaining the possibility of equimolar reaction between the components resulting in the formation of $[\text{HSO}_3]^+[\text{ClO}_4]^-$ compounds, i.e. a compound in which the perchloric acid assumes the role of an acid and the sulfuric anhydride - the role of a base. The derivation of such a compound would serve as the best proof for the existence of an $\text{SO}_3 \text{H}^+$ ion. The results obtained are tabulated. Two USA references (1938 and 1950). Table.

Institution : Chemical Technological Institute, Ivanovo

Presented by : Academician A. N. Frumkin, December 11, 1954

Spryskov, A.A.
APPROVED FOR RELEASE: 08/25/2000 CIA-RDP86-00513R001652730002-5
USSR/ Analytical Chemistry - Analysis of Organic Compounds

Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 12156

Author : Spryskov A.A., Yerykalov Yu.G.

Title : Quantitative Determination of Isomers of Dichlorobenzenes

Orig Pub : Zh. analit. khimii, 1956, 11, No 4, 492-494

Abstract : After determination of p-dichlorobenzene (I) by thermal method, and m-dichlorobenzene (II) by the bromide-bromate method developed by the authors specifically for II, o-dichlorobenzene (III) can be determined, in mixtures of the three isomers, by difference. After ascertaining the content in I, from the solidification point of the mixture under investigation, this mixture is subjected to nitration and reduction, in order to determine II by bromination. Sample of the substance being analyzed (1.5 g) is mixed with an equal weight of water, there are added, after cooling, dropwise and within 30 minutes, 15 g HNO_3 (Sp. Gr. 1.5), after $\frac{1}{2}$ hour the mixture

USSR/ Analytical Chemistry - Analysis of Organic Substances

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 12156

is poured into 50 ml water and the product is washed, in a separatory funnel, until the water wash is neutral. The nitro-compound thus obtained is mixed, in a wide test tube fitted with a glass-tube extension connected through a ground joint, which serves as an air condenser, with 6 g Zn dust, and 30-40 ml HCl (Sp. Gr. 1.18) are added carefully with cooling until all the Zn dust is dissolved, after which the contents of the test tube are boiled, over a wire gauze, for 1 hour. The hot solution is poured into 250-300 ml of water, filtered into a 500 ml measuring flask, 60 ml HCl (Sp. Gr. 1.18) are added and the flask is filled to the mark. 100 ml of this solution are titrated with NaNO_2 using tropaeolin OO as indicator (to determine the total amount of amines formed by nitration and reduction of I-III) (S). An additional 25 ml of the solution are combined with 0.1 N KBr - KBrO_3 until the solution acquires a distinct yellow coloration, after which the

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USSR/ Analytical Chemistry - Analysis of Organic Substances

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Abs Jour : Referat Zhur - Khimiya, No 4, 1957, 12156

mixture is allowed to stand for 30 minutes in a sealed vessel. Thereafter 2 g KI are added and after 5 minutes the I_2 is titrated with 0.1 N solution $Na_2S_2O_3$ in the presence of starch (to determine the amount of dichloraniline formed from I and III) (S_2). Amount of dichloraniline formed from II is $S_1 - S \cdot 25/100 - S_2$, hence the content of II in the mixture is: (in %) $S_1 \cdot 100 / S - 100/25$. Since the content of I in the mixture is known from the solidification point the content of III can be calculated as the difference. Error in determination of each inomer is 1% of the sum of isomers. The described procedure has been checked with compounded mixtures.

Card 3/3

Spryskov, A. A.

Distr: 4E4j/4E3d/4E2c(3)7
✓ Determination of dichlorobenzene isomers. A. A.
Spryskov and Yu. G. Brykalov. J. Anal. Chem. U.S.S.R.
14, 521-3 (1956) (English translation).—See C.A. 51, 15435b.
B. M. R.

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Spryskov, A. A.

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Sulfonation reaction. XXXVIII. Preparation and properties of 1,8-naphthalenedisulfonic acid. B. I. Karavaev and A. A. Spryskov (Chem. Technol. Inst., Ivanovo). *Zhur. Vsesoyuzn. Khim.* 20, 601-4 (1956); cf. C.A. 50, 63201. Diazotization of 24 g. 1,8-naphthylaminesulfonic acid in conventional procedure gave the ppt. of the diazonium salt which was filtered off, washed and treated with a soln. of 25 g. $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and 3.5 g. S in 50 ml. 10% NaOH at 5° ; after 3 hrs. the soln. was acidified with HCl, heated to remove H_2S , filtered and treated with BaCl_2 , yielding a ppt. of Ba salt which heated with Na_2CO_3 gave the di-Na salt of the disulfide disulfonic acid, which treated with KMnO_4 [cf. Ger. 70,206] gave 54% di-Na 1,8-naphthalenedisulfonate. Heating the salt with PCl_5 or P_2O_5 gave 35-55% corresponding anhydride. An 85% yield results when 10 g. di-Na salt is heated 2.5 hrs. at $55-60^\circ$ with 30 ml. ClSO_3H ; the anhydride m. 232° (from CH_2Cl_2). This heated with 25% NH_4OH gave the NH_4 salt of the monoamide, very sol. in H_2O , which with BaCl_2 gave the Ba salt of the monoamide, sparingly sol. in cold H_2O , sol. hot; this salt contains 4.5 moles H_2O (lost at 110°). Treatment with the calcd. amt. of H_2SO_4 and evapn. gave the anhydride of naphthalene-1,8-disulfonic acid. The latter heated with 80% EtOH until completely dissolved, then evapd. gave colorless needles of 1,8-naphthalenedisulfonic acid (from 10% HCl) contg. 4 moles H_2O . The acid heated at $56-122^\circ$ 1-5 hrs. with H_2O is hydrolyzed rather rapidly to the hydrocarbon and the monosulfonic acid; with 38% H_2SO_4 the hydrolysis is rapid even at 50° and is complete in 6 hrs. at 100° . The relative insoly. of the anhydride of the 1,8-disulfonic acid might be used for its isolation from the direct sulfonation mixts., provided

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KARAVASH, B. I. SORVSKOV, A. A.
 that at least 5% yield is present. Sulfonation of 1-naph-
 thalenesulfonic acid with 92% H_2SO_4 3-60 days or with
 100% H_2SO_4 with $HgSO_4$ at 0° , followed by treatment of
 the mixt. with 100% H_2SO_4 in excess to form the above an-
 hydride, followed by pouring into H_2O gave a temporary
 ppt. of the anhydride of the 1,5-disulfonic acid; no insol.
 anhydride of the 1,8-disulfonic acid was detected, nor was it
 found after sulfonation with $ClSO_3H$ of $1-C_{10}H_7SO_3Cl$ at
 -8° . The difficulty of introduction of *peri*-sulfonic acid
 groups is ascribed to steric hindrance. G. M. K.

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Spryskov, A.A.

Sulfonation reaction. XXXIX. Hydrolysis and isomerization of naphthalenetrisulfonic acids. B. I. Karavay and A. A. Spryskov (Chem. Technol. Inst., Ivanovo). Zhur. Doklady Akad. Nauk, 26, 2002-5 (1956); cf. C.A. 51, 2682g. The following order of decreasing stability to hydrolysis was found for the trisulfonic acids of $C_{10}H_6$ which are formed by direct sulfonation of the hydrocarbon, the hydrolysis being run at 101° in 75-8% H_2SO_4 : 1,3,7-, 1,3,8-, and 1,3,5-trisulfonic acids. These, treated with 98% or 100% H_2SO_4 , were subjected to isomerization in contact with the acids at 101° for up to 600 hrs. Starting with any of the 3 isomers the system tends to approach an equilibrium, about 83% 1,3,5-isomer, which is the most stable one, and its rate of formation appears to be greater than that of the 1,3,7-isomer. In the conventional sulfonation of $C_{10}H_6$ to trisulfonic acid, such as in production of H-acid, the mixture does not contain any tetrasulfonic acids and about 72% 1,3,5-trisulfonic acid is formed. G. M. Kosolapoff

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SPRYSKAR, A. A.

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~~Sulfonation reaction. XL. Determination of benzenedi-~~
~~sulfonic acids? A. A. Spryskov and S. P. Starkov (Chem.~~
~~Technol. Inst. France) Zh. Obshchei Khim. 26, 2607-~~
~~11(1956); cf. C.A. 47, 8709c; 51, 2682g. Semiquant.~~
~~detns. of soly. are reported for salts of o-, m- and p-benzenedi-~~
~~sulfonic acid salts with 18 typical amines. On the basis of~~
~~these, the following procedures are suitable for detn. of disul-~~
~~monic acids: for the ortho isomer the sample is neutralized~~
~~with 0.5N NaOH, to phenolphthalein and treated with N~~
~~PhNH₂·HCl, the ppt. of the salt with o-disulfonic acid~~
~~being then sepd. and titrated while boiling with NaOH to~~
~~phenolphthalein end point. The sum of the ortho and para-~~
~~isomers is detd. similarly by the use of 2-naphthylamine~~
~~salt which is sepd. after chilling the mixt. in ice, as it was~~
~~with the ortho isomer above. For detn. of the para isomer~~
~~in the absence of ortho isomer the sample is neutralized with~~
~~Ba(OH)₂, excess Ba is removed with H₂SO₄, and the acid~~
~~is pptd. as benzidine salt which is sepd. and back titrated~~
~~with NaOH as above. The method is usable in the presence~~
~~of mono- and trisulfonic acids. G. M. Kosolapoff~~

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SPRYSKOV, A. A.

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~~Sulfonation reaction. XI. Hydrolysis and sulfonation of benzenedisulfonic acids. A. A. Spryskov and S. P. Starikov (Chem. Technol. Inst. Ivanovo, Zhur. Obshchei Khim. 26, 2502-4 (1956); cf. C.A. 51, 4214g. -- It is shown that hydrolysis of isomeric $C_6H_4(SO_3H)_2$ or $C_6H_4(CO_2H)_2$ proceeds at different rates. The *p*-isomers are most resistant to hydrolysis, *m*-isomers are intermediate, and *o*-isomers are most readily hydrolyzed. *o*- $C_6H_4(SO_3H)_2$ begins to hydrolyze noticeably in 80% H_2SO_4 at somewhat under 180° , while the *m*-isomer requires 195° , and *p*-isomer 205° . The *m*-isomer is sulfonated by 60% oleum at a good rate at 200° and very rapidly at 230° . The *o*- and *p*-isomers~~

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heated with oleum to $200-30^\circ$ undergo but slow change and no products of either isomerization or sulfonation can be isolated. When *p*- $C_6H_4(SO_3Cl)_2$ is heated briefly with oleum to 228° no change takes place, but after 24 hrs. its m.p. drops to 104° , although recrystn. again yields the original substance, m. $136-7^\circ$. The *o*-isomer is unchanged after brief heating with oleum but long heating yields noncrystg. products.

G. M. Kozlovoff

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AUTHORS: Spryskov, A. A., and Yakovleva, T. I.

TITLE: Orientation during Displacement in the Aromatic Series. Part 1. Sulfonation of m-Toluenesulfonic Acid (K oriyehtatsii pri zame-shchenii v aromatcheskom ryadu. 1. Sul'firovaniye m-toluolsul'-fokisloty)

PERIODICAL: Zhurnal Obsheey Khimii, 1957, Vol. 27, No. 1, pp. 239-244 (U.S.S.R.)

ABSTRACT: It is known that the orientation of a newly incoming substitute during the displacement in a benzene ring is affected by the reactivity of the given compound and reaction condition, i. e. temperature, activity of attacking agent and time of reaction. The effect of these very factors on the orientation of a newly incoming sulfo-group was investigated during m-toluene-sulfonic acid sulfonation experiments. Instead of the anticipated 1,2,5- and 1,3,5-toluenedisulfonic acids, the authors obtained a 1,3,5-isomer (the sulfo-group is oriented in meta-position relative to the methyl group) which was found to be a kinetically highly stable isomer. The ortho-, para-orienting effect of the methyl

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Orientation during Displacement in the Aromatic Series

group in toluene was seen to become weaker in m-toluenesulfonic acid as a result of the deactivation of the nucleus of the sulfo-group. Sulfonation of m-toluenesulfonic acid results in the formation of a more stable meta-isomer (1,3,5-toluenedisulfonic acid). An increase in temperature and activity of the sulfonating agent increase the amount of the isomer. An increase in reaction period has the same effect as temperature and activity increases. The results of sulfonation with various agents and at different temperatures are tabulated. Six tables, 1 graph. There are 7 references, of which 2 are Slavic.

ASSOCIATION: The Ivanov Chemical-Technological Institute (Ivanovskiy Khimiko-Tekhnologicheskii Institut)

PRESENTED BY:

SUBMITTED: January 30, 1956

AVAILABLE:

Card 2/2

SPRYSKOV, A.A.

Orientation in substitution in aromatic nucleus. II.
Electron shifts in the benzene ring. A. A. Spryskov, Zhur.
Obshchei Khim. 27, 1949-50 (1957), Cf. C.A. 51, 8038k,
12847c.—Aromatic orientation is discussed semiquanti-
tatively on the basis of shifts of electron densities in the C₆H₆
ring. G. M. Kosolapoff

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SPRYSKOV, A.A.; STARKOV, S.P.

Sulfonation reaction. Part 43: Sulfonation of benzene to disulfonic acids. Zhur.ob.khim. 27 no.10:2780-2786 0 '57. (MIRA 11:4)

1.Ivanovskiy khimiko-tekhnologicheskii institut.
(Benzene) (Sulfonation) (Fulfonic acids)

Spryskov, A. A.

79-11-33/36

AUTHORS:

Starkov, S. P., Spryskov, A. A.

TITLE:

Investigation of the Sulfonation Reaction
(Izucheniye reaktivov sulfirovaniya).
XLIV. The Isomerization of Benzene Disulfonic Acids
(XLIV. Izomerizatsiya benzoildisulfonata).

PERIODICAL:

Zhurnal Obshchey Khimii, 1957, Vol. 27, No. 11,
pp. 3067-3071 (USSR)

ABSTRACT:

The m- and p-benzene disulfonic acids forming on sulfonation of benzene at a sufficiently high temperature in an aqueous sulfuric medium pass one into the other until a certain equilibrium between them is attained. In connection with some foreign papers (Hollmann and Pollack) the object of the present paper was to obtain exact details on the state of equilibrium between the meta- and para-isomers, on the isomerization of o-benzene disulfonic acid, on the dependence of the speed of isomerization on the concentration of the sulfuric acid and other conditions of equilibrium. Thus the influence of the concentration of sulfuric acid upon the time of isomerization of the m-benzene disulfonic acid was investigated. With an increase in concentration of 90 to 100 % the speed of isomerization at 206-233°C decreases; it is

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Investigation of the Sulfonation Reaction.

79-11-03/56

XLIV. The Isomerization of Benzene Disulfonic Acids

highest at 90% (206°C) and at 87% (235°C). The isomerization of the o-benzene disulfonic acid at 233°C proceeds rapidly, so that after 2,5 hours only 7% of the raw product remain. The isomerization of the m- and p-benzene disulfonic acids proceeds slowly. By heating of the meta- and para isomer at 235°C in the course of 200 hours in the presence of 87% sulfuric acid a state of equilibrium is practically attained between the isomers (66,3% meta- and 33,7% para isomer). There are 3 tables, and 6 references, 4 of which are Slavic.

ASSOCIATION: Ivanovo Chemical-Technological Institute
(Ivanovskiy Khimiko - tekhnologicheskii institut).

SUBMITTED: October 17, 1956

AVAILABLE: Library of Congress

1. Benzene disulfonic acids - Isomerism

Card 2/2

SPRYSKOV, A. A.
AUTHORS: Spryskov, A. A., Kachurin, O. I.

79-11-34/56

TITLE: Investigation of the Sulfonation Reaction
(Izucheniye reaktsii sul'firovaniya).
XLV. Concerning the Determination of the Isomeric
Chlorobenzene Sulfonic Acids (XLV. K opredeleniyu
izomernykh khlorbenzolsul'fokislot).

PERIODICAL: Zhurnal Obshchey Khimii, 1957, Vol. 27, Nr 11,
pp. 3072-3075, (USSR)

ABSTRACT: Of three isomeric chlorobenzene sulfonic acids only
the p-chlorobenzene sulfonic acid was found in direct
sulfonation of chlorobenzene. No method was hitherto worked
out for determining the o- or m-chlorobenzene sulfonic acids
in the sulfomixture, so that the absence of these two isomers
is not yet quite proved. Thus their determination in the
sulfomixtures is indispensable for the investigation of the
process of sulfonation of chlorobenzene. The m-isomer can be
determined in the mixture by substitution of chlorine in the
chlorobenzene sulfonic acid by an alkylamino group. In the
bromination of the resulting mixture of isomeric N-alkyl-
aminosulfonic acids the sulfo group, which is in ortho- or
paraposition to the amino group, is separated by bromine.

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Investigation of the Sulfonation Reaction.
XLV. Concerning the Determination of the Isomeric
Chlorobenzene Sulfonic Acids

79-11-34/56

The quantity of the meta isomer can be found by determination of the total quantity of amine after bromination and the quantity of the separated sulfuric acid. The para isomer in the sulfomixture can be found by the quantity of the meta isomer. The para isomer in the sulfomixture can be obtained with the aid of the thermal analysis in the mixture of the chlorobenzene-sulfochlorides. The melting point of the p-chlorobenzene sulfochloride is 53°C, of the ortho isomer 28,5°C, but the meta isomer does not solidify in the cooled mixture. The m-chlorobenzene sulfochloride crystallizes at - 26,3°C. The fusion curve of the triple sulfochloride mixtures found by the authors gives the determination of the para isomer in the mixture. There are 1 figure, 3 tables, and 4 references.

ASSOCIATION: Ivanovo Chemical-Technological Institute (Ivanovskiy
Khimiko - tekhnologicheskii institut).

SUBMITTED: November 17, 1956

AVAILABLE: Library of Congress

Card 2/2 1. Chlorobenzene sulfonic acids - Determination

SPRYSKOV, A.A.; SOLODUSHENKOV, S.N.; KLYUYEV, V.N.

Preparation of symmetric 4,4'-dinitrocarbanilides. Zhur.prikl.khim.
30 no.7:1065-1070 J1 '57. (MIRA 10:10)

1.Ivanovskiy khimiko-tekhnologicheskij institut.
(Carbanilide)

Spryskov, A. P.

Synthesis and uses of carbanilide derivatives. II. Synthesis of some nitro- and aminocarbanilides. S. N. Solodushenkov, V. N. Klyuev, and A. A. Spryskov (Chem. Technol. Inst., Ivanovo). *Zhur. Prirod. Khim.* 30, 1381-7 (1957); cf. C.A. 52, 281g. Sym. and unsym. substituted mono- and dinitrocarbanilides were synthesized from 2-methoxy-4-nitrophenyl isocyanate (I) and aminocarbanilides from Ac derivs. of p-phenylenediamine and from aminoazobenzene. Bubbling COCl_2 4-6 hrs. through a soln. (40-5%) of 34 g. 2-methoxy-4-nitroaniline (II) in 600 ml. dry PhMe contg. 21 g. Na_2CO_3 gave 58% I, m. 114.5-15° (dry PhMe). Derivs. of 2,2'-dimethoxycarbanilide were synthesized by refluxing 30 min. PhMe solns. of equiv. amts. of I and II giving on cooling 4,4'-(NO_2)₂ deriv., m. 275°; refluxing I 1-1.5 hrs. in PhMe with an equiv. amt. of o-anisidine pptd. on cooling 4- NO_2 deriv., m. 203.5° (80% AcOH). A hot soln. of I in PhMe added slowly to a PhMe soln. contg. equiv. amts. of 2,4-dimethoxy-1-aminotoluene and refluxed 30-40 min. gave on cooling green-yellow leaflets of 4-nitro-2,2',4'-trimethoxy-5'-methycarbanilide (about 100%), m. 211° (80% AcOH). Acetylation of 2-chloro-4-nitroaniline followed by reduction with cast iron filings at 75° yielded 90% N'-acetyl-2-chloro-1,4-phenylenediamine, m. 133°, which in aq. NaOAc reacted with COCl_2 at 30-5° yielding 94-95% 4,4'-diacetamido-3,3'-dichlorocarbanilide (III), m. 299.5° (glacial AcOH). III is subject to several types of hydrolysis. Different conditions were investigated. Hydrolyzed 7 hrs. in 50% H_2SO_4 at 77° III gave 88% 4,4'-(H_2N)₂ deriv., m. about 247° (decompn.). Acetylation of II followed by reduction gave 2-methoxy-N'-acetyl-1,4-phenylenediamine which in Na_2CO_3 soln. reacted with COCl_2

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SOLODUSHENKOV, S. N.; KLYUEV, U. N.; SPYTSKOV, A. A.

yielding practically 100% 4,4'-diacetamido-3,3'-dimethoxycarbanilide (IV), m. 251.5-3° (dl), AcOH). Hydrolysis of IV in hot HCl (1:1) gave on cooling the HCl salt of the 4,4'-(H₂N)₂ deriv., m. 228° (decompn.). The base, m. 191°, was pptd. from a warm soln. of the salt with NH₄OH. Acetylation, nitration, and reduction of 2-methoxy-5-chloroaniline gave N'-acetyl-2-methoxy-5-chloro-1,4-phenylenediamine, m. 150-3°, which with COCl₂ at 35-40° gave 81% 4,4'-diacetamido-3,3'-dichloro-5,5'-dimethoxycarbanilide, m. 231.5-2.5° (pyridine). This hydrolyzed 10-15 min. in boiling 20% HCl gave the 4,4'-(H₂N)₂ deriv., distd. without m. 315°. Aminoazobenzene in C₆H₆ with COCl₂ yielded 32.7% bis(azo dye), m. 258° (decompn.); on reduction and steam distn. 87% 4,4'-diaminocarbanilide was obtained, did not m. 316°.

I. Benowitz

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Spryskov, A.A.

Synthesis and uses of carbanilide derivatives. III.
Preparation of aminocarbanilides. 7 Y. N. Klyuev, A. A. Spryskov, and B. N. Solodushenkov (Chem.-Technol. Inst., Ivanovo). *Zhur. Priklad. Khim.* 30, 1872-7 (1987); *cf. C.A.* 52, 5321s. — Twelve new amino carbanilides were synthesized by reduction of the nitrocarbanilides previously prepd. (*loc. cit.*) with Zn dust in HCl and with Fe in AcOH. To a mixt. of the nitro deriv. and aq. EtOH, concd. HCl was added and then Zn dust over a period of several hrs. The following diamino derivs. were thus obtained from the corresponding dinitro compds.: 4,4'-diamino-3,2',5,5'-tetramethylcarbanilide, yield 48.5%, not melting up to 315°; 4,4'-diamino-2,2'-dimethyl-5,5'-dichlorocarbanilide, yield 63.5%, not melting up to 315°; 4,4'-diamino-2,2'-diethoxy-5,5'-dimethylcarbanilide, m. 184° (50% EtOH) (decompn.); 4,4'-diamino-2,2',5,5'-tetraethoxycarbanilide, yield 60%, m. 199° (EtOH). The following derivs. were prepd. by addg. gradually the corresponding nitro derivs. to a mixt. of Fe shavings and aq. AcOH, previously digested 1 hr. with stirring at 90-5°, and continuing the digestion at this temp. for several hrs.: 4,4'-diamino-2,2'-dichlorocarbanilide, m. 287°; 4,4'-diamino-2,2'-dimethoxycarbanilide, yield 50-60%, m. 192°; 4,4'-diamino-2,2',5,5'-tetramethoxycarbanilide, yield 45-50%, m. 236° (C₆H₆); 4,4'-diamino-2,2'-dimethoxy-5,5'-dimethylcarbanilide, yield 50%, m. 230° (MeOH) (decompn.); 4,4'-diamino-2,2'-dimethoxy-5,5'-dichlorocarbanilide, yield 70%, m. 254-6° (MeOH); 4-amino-2,2',4'-trimethoxy-5'-methylcarbanilide, yield 82%, m. 175°; 4,4'-diamino-2,2',5,5'-tetrachlorocarbanilide, yield 61%, not melting up to 315° (the latter compd. was also obtained in a 58% yield by refluxing the nitro deriv. with Na₂S 1-1.5 hrs.); 4-amino-2,2'-dimethoxycarbanilide, yield 20-25%, m. 166° (EtOH).
 Distr: 4E4j/4E2c(j) I. Bencowitz

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AUTHORS: Spryskov, A. A., Kachurin, O. I. 153 -58-1-15/29

TITLE: Investigation of the Sulphonization-Reaction (Izucheniye reaktsii sul'firovaniya). XLVIII. Quantitative Determination of Isomeric Chlorobenzene-Sulfo Acids (XLVIII. Kolichestvennoye opredeleniye izomernykh khlorbenzolsul'fokislot)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 1, pp. 97-99 (USSR)

ABSTRACT: Both quantitative and qualitative elaborated methods of determination of the aforesaid acids in a mixture which is formed due to an immediate chlorobenzene-sulphonization, are lacking up till now. Only the p-chlorobenzene-sulfo acid was found in it (ref. 1). The absence of other isomers in mixtures formed under various conditions of sulphonization remains unproved. The method of determination of the meta-isomer was based on the substitution-reaction of chlorine by the methyl-amino-group in the chlorobenzene-sulfo acid under the action of methyl amine (ref. 2 by the authors). The formed mixture of the isomeric N-methyl-aniline-sulfo acids is analyzed by means of bromination, in which case the

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Investigation of the Sulphonization-Reaction.

153-58-1-15/29

XLVIII. Quantitative Determination of Isomeric Chlorobenzene-Sulfo Acids

sulfo group - which is in an o- or p-position to the amino-group - is quantitatively replaced by bromine. The content of the meta-isomer is determined by means of the determination of the total quantity of amine from the consumption of bromine and according to the H_2SO_4 separated from the ortho- and para-isomers by means of the method of weight. The para-isomer is determined in the sulfo-mixture by means of the thermal analysis of the mixture of chlorobenzene-sulfochlorides (ref. 2). The ortho-isomer is determined from the difference. A prescription of analysis follows. As mentioned above, the total quantity of sulfo acids can be calculated from the quantity of bromine consumed for bromination. The quantity of the o- and p-isomers is determined from the quantity of barium sulfate. If the quantity of bromine consumed is expressed as a volume of a 0,1 n-solution of the bromide-bromate, the result may be calculated according to the formula

$$\frac{60\ 000 \cdot 100 \cdot S \cdot K_1}{233,4/K_1 3(25-5)+K_2(a-b)} = \sum \text{ of the o- and p-isomers}$$

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Investigation of the Sulphonization-Reaction.

153-58-1-15/29

XLVIII. Quantitative Determination of Isomeric Chlorobenzene-Sulfo Acids

in % of the amount of the sulfo-acids, in which case S - is the weight of the BaSO_4 , K_1 and K_2 coefficients to the rigorous 0,3 and 0,1 n-solutions of the bromide-bromate and a as well as b are ml-numbers of the latter solution consumed for the titration in a operational and control test. m- and o-isomers are determined from the difference between the amount of all isomers and of the ortho- and para-amount, p-isomer from the results of thermal analysis. The checking of the results obtained with artificially produced mixtures of pure isomers (table) showed deviations which rarely exceeded 1% of the isomeric amount. There are 1 table and 2 references, 1 of which is Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut, Kafedra organicheskoy khimii (Ivanovo Chemical Technological Institute, Chair for Organic Chemistry)

SUBMITTED: September 21, 1957

Card 3/3

5(3)

007/153-58-5-8/28

AUTHORS: Kachurin, O. I., Spryskov, A. A.

TITLE: Investigation of the Sulfonation Reaction (Izucheniye reaktsii sul'firovaniya) LI. Isomerization of Chloro Benzene Sulfo Acids (LI. Izomerizatsiya khlorbenzolsul'fokislot)

PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 5, pp 52-57 (USSR)

ABSTRACT: Earlier (Ref 1) the authors had proved that the ortho-chloro benzene sulfo acid together with the p-isomer can be formed by the action of sulfur trioxide on chloro benzene at low temperatures. Within the range of from room temperature to 150°C the para acid is formed practically alone on the action of any sulfonizing agents on chloro benzene. At higher temperatures p- and m-isomer mixtures are formed in which the m-isomer can amount up to 55%. The problem mentioned in the subtitle was investigated with m- and p-sulfo acids. Their isomerization takes place by the hydrolysis of the acids and the resulfurization of the chloro benzene formed. It was proved that the hydrolysis of the p-isomeric sulfo acids in a sulfuric acid is observed at about 150°C. Table 1 shows the experimental results. At

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SOV/153-58-5-8/28

Investigation of the Sulfonation Reaction. LI. Isomerization of Chloro Benzene Sulfo Acids

higher temperatures the transformation of the p-isomer into the m-isomer becomes possible. At 168° the hydrolysis of the latter is also observed. At the same time benzene sulfo acid was hydrolyzed under the same conditions. The chlorine atom in a o- and p-position to the sulfo group in the benzene nucleus activates the molecule to the hydrolysis reaction. The latter is an electrophilic reaction. Chlorine in a m-position has a deactivating effect. As the isomerization takes place at an almost unchanged concentration of sulfuric acid and water it may be regarded as a reversible pseudomolecular process. From its equation the kinetic equation and the equilibrium constant between the isomers is derived. The experimental results mentioned in table 2 show the effect of the amount of sulfuric acid upon the rate of isomerization. Table 3 gives the results of the experiments carried out at 3 different temperatures (185, 204 and 220°). They show that the equilibrium constant changes little with temperature. Figures 1 and 2 show the linear dependence of the quantity $\log(1-F)$ upon time, with F denoting the ratio of the current concentration (x_p or x_m) of

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Investigation of the Sulfonation Reaction. LI. Isomerization of Chloro
Benzene Sulfo Acids

the isomer formed in the reaction and its equilibrium concentration. The average value of the constants for each temperature was found according to the method of the least squares. The results of the calculations are given in table 4. Figure 3 gives the linear dependence of the natural logarithms of the velocity constants upon the reciprocal temperature. The results obtained made possible the calculation of the values of the activation energies of the isomerization process of each isomer according to the theory of the least squares. Finally the temperature coefficient of the reaction was calculated. In an equilibrium mixture about 54% of the m- and 46% of the p-isomer are contained. At 220° a state close to the equilibrium is obtained after 27 hours.

There are 3 figures, 5 tables, and 2 Soviet references.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii Institut, Kafedra organicheskoy khimii (Ivanovo Chemo-Technological Institute, Chair of Organic Chemistry)

Card 3/4

SOV/153-58-6-8/22

5(3)

AUTHOR:

Spryskov, A. A.

TITLE:

Study of the Sulfuration Reaction (Izucheniye reaktsii sul'firovaniya). XLIX. Determination of the Isomeric Toluene-sulfo Acids in Their Mixture (XLIX. Opreddeniye izomernykh toluolsul'fokislot v ikh smesi)

PERIODICAL:

Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1958, Nr 6, pp 42-46 (USSR)

ABSTRACT:

The acids mentioned in the subtitle are quantitatively determined in a sulfo mixture (obtained from toluene sulfuration) by means of a thermal method (Ref 1). This method is cumbersome, if not impossible, with a higher m-isomer content and in ternary systems, as the crystallization heat of the toluene-sulfo-chlorides has a low value. The author has developed a chemical determination method for m-toluene-sulfo acid, which, together with the above thermal method for the p-isomer, facilitates the analysis of any given mixture. The new method is based on the following reactions: the toluene-sulfo-chloride mixture is nitrated. The resulting nitro-toluene-sulfo-chlorides are saponified and reduced. By means of a diazotization of part of the solution the total quantity of toluidine-sulfo

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SOV/153-58-6-8/22

Study of the Sulfuration Reaction. XLIX. Determination of the Isomeric Toluene-sulfo Acids in Their Mixture

acids is determined. After treatment with bromine the remainder of the solution splits off sulphuric acid from the 4- and 6-amino-toluene-3-sulfo acids. The latter had been formed from the o- and p-toluene-sulfo acids. The toluidine-sulfo acids formed from the o- and p-toluene-sulfo acids do not permit the splitting-off of sulfo groups by means of bromination. The H_2SO_4 separated out is determined with regard to weight. From this the m-toluene-sulfo acid content is obtained. In an experimental part the usual data are presented. The method was tested with pure toluene-sulfo acids as well as with artificial mixtures of pure toluene-sulfo-chlorides. Table 1 lists the determination results of the isomeric acids in such mixtures; table 2 - the transformation of p-toluene-sulfamide into chloride; table 3 the effect of HSO_3Cl on p-toluene-sulfo-chloride. P. T. Pestova participated in the work. There are 3 tables and 5 references, 2 of which are Soviet.

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SOV/153-58-6-8/22

Study of the Sulfuration Reaction. XLIX. Determination of the Isomeric
Toluene-sulfo Acids in Their Mixture

ASSOCIATION: Kafedra organicheskoy khimii; Ivanovskiy khimiko-tekhnologicheskii institut
(Chair of Organic Chemistry; Ivanovo Chemo-technological Institute)

SUBMITTED: December 25, 1957

Card 3/3

SPRYSKOV, A. A.

79-1-39/63

AUTHORS: Spryskov, A. A. , Kuz'mina, Yu. L.
 TITLE: Investigation of the Sulfonation Reaction (Izucheniye reaktsii sul'firovaniya) XLVI. The Equilibrium Between Toluene-Trisulfonic Acid and Its Chlorine Anhydride (XLVI. Ravnovesiye mezhdu toluoltrisol'fokislotoy i yeye khlorangidridom)
 PERIODICAL: Zhurnal Obshchey Khimii, 1958, Vol.28, Nr 1, pp.184-187(USSR)
 ABSTRACT: It was shown earlier (reference 1) that between sulfonic acids and their chlorine anhydrides in a mixture consisting of sulfuric and chlorosulfonic acid the state of equilibrium sets in after the process of reaction $RSO_2Cl + H_2SO_4 \rightleftharpoons RSO_3H + HSO_3Cl$. It was pointed out that the constant-quantities of the state of equilibrium for the di- and tri-sulfo derivatives are as a rule higher than for the mono-sulfo derivatives. The present paper describes the equilibrium investigations for a case, concerning the polysulfo derivatives - 2,4,6-toluene-trisulfochloride and the corresponding sulfonic acid in a mixture consisting of sulfuric and chlorosulfonic acid. The chloride was added to this mixture of various composition, in small containers, with a good shutter. After the solution of the tri-

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79-1-39/63

Investigation of the Sulfonation Reaction. XLVI. The Equilibrium Between Toluene-Trisulfonic Acid and Its Chlorine Anhydride

chloride the reaction mixtures were cast on ice. The liberated trichloride was filtered, washed, dried and weighed. The reaction mixtures were left resting for 10 hours, as the tests showed that at 80°C this period is almost sufficient for the setting in of the state of equilibrium. (The calculation of the equilibrium constant for the trisulfo-substituted compounds of toluene is given in equations and 2 tables). It is shown that starting from polysulfonic acids larger quantities of chlorosulfonic acid are needed for every sulfo-group for obtaining the same yields than when starting from mono-sulfonic acids. Sodium sulfonates demand more chlorosulfonic acid for the same yields of chloride than the free sulfonic acids. There are 3 references, all of which are Slavic.

ASSOCIATION: **Ivanovo Chemical-technological and Ivanovo State Medical Institutes**
(Ivanovskiy khimiko-tehnologicheskii institut i Ivanovskiy gosudarstvennyy meditsinskiy institut)

SUBMITTED: December 17, 1956

AVAILABLE: Library of Congress

Card 2/2 1. Chemistry 2. Sulfones-Reactions

AUTHORS: Spryskov, A. A., Yerykalov, Yu. G. SOW/79-28-6-47/63

TITLE: On the Orientation of the Substitution in the Aromatic Series
(K oriyehtatsii pri zameshchenii v aromatische kom ryadu) III.
The Isomerization of Dichlorobenzenes (III. Izomerizatsiya
dikhlorobenzolov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6,
pp. 1637 - 1642 (USSR)

ABSTRACT: The aim of the present paper is to investigate the isomerization
of dichlorobenzenes and to obtain states of equilibrium among
the isomers on various conditions. Proceeding from any dichloro-
benzene a state of equilibrium among the isomers was obtained
on its heating with aluminum chloride at 160°. In the equilibrium
mixture were 16% ortho-, 30% para- and 54% meta isomers found. The
velocity of the isomerization process depends on the amount of
aluminum chloride. Besides this isomerization also a disproportion-
ing takes place which in the experiments, on a heating up to
160° for 50 hours, yielded about 1,6% monochlorobenzene and up to
2,8% of a resinous product. The results of the experiments tend
to show that on the heating with aluminum chloride a dehalogenation

Card 1/3

On the Orientation of the Substitution in the Aromatic|DV/79-28-6-47/63
Series.III. The Isomerization of Dichlorobenzenes

of dichlorobenzene takes place under the formation of monochlorobenzene as well as a formation of chlorine. The latter chlorinates monochlorobenzene and forms a mixture of dichloro-substituteds. The process of dehalogenation is represented by the given scheme. Hydrogen chloride forms in this system by conversion of aluminum chloride with a small amount of air humidity. Thus this chlorination reaction in the presence of a catalyst is reversible. However, the velocity of the counterreaction at low temperatures is so low that the halogenation reaction can practically not be reversed. With increased temperature also the velocity of the reversible conversion increases. It becomes an isomerization and it becomes possible to obtain a state of equilibrium. There are 1 figure, 4 tables and 11 references, 4 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut (Ivanovo Chemical-Technological Institute)

SUBMITTED: May 11, 1957
Card 2/3

On the Orientation of the Substitution in the Aromatic Series. III. The Isomerization of Dichlorobenzenes

SOV/9-28-6-47/63

1. Chlorobenzenes--Isomerism

Card 3/3

AUTHORS: Spryskov, A. A., Kachurin, O. I. 30V/79-28-6-48/63

TITLE: Investigation of the Sulfonation Reaction (Izucheniye reaktsii sul'firovaniya) XLVII. The Investigation of the Hydrolysis of Chlorobenzenesulfo Acid According to the Method of Radioactive Indicators (XLVII. Ob izuchenii gidroliza khlorbenzolsul'fokisloty metodom radioaktivnykh indikatorov)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 6, pp. 1642 - 1646 (USSR)

ABSTRACT: As is known the reaction velocity of the hydrolysis of sulfo acids depends on the temperature, the nature of the mineral acid present, its concentration and the concentration of the sulfo acid itself (Ref 1). Thus with an increase of the concentration of sulfuric acid in the reaction mixture also the velocity of the hydrolysis of sulfo acids increases. It was, however, shown that in the case of an increase of the concentration of sulfuric acid from 90-100% the isomerization of the m-benzenedisulfo acid, which takes place via hydrolysis, slows down. It was found in the investigation of the hydrolysis of 1,3,6-naphthalenetrisulfo acid at 180° (Ref 3) that with an increase of the concentration of sulfuric acid up to 87,6% also the amount of desulfonated sulfo acid increases, but

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Investigation of the Sulfonation Reaction. XLVII. The ³⁵S/79-28-6-48/63
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that it decreases when the concentration reaches 95,%. This decrease is certainly connected with the resulfonation reaction of the product of hydrolysis, the velocity of which in the case of an increase of the concentration of sulfuric acid highly increases. Thus this resulfonation reaction hampers the investigation of the influence exerted by high concentrations of sulfuric acid on the velocity of hydrolysis as it had earlier always been estimated according to the amount of the product of hydrolysis or according to the quantitative increase of sulfuric acid in the mixture. In order to remove this hindrance the authors used radioactive sulfuric acid with the isotope S^{35} . The chlorobenzenesulfo acid mixed with this acid is only hydrolyzed at higher temperature while the residual sulfo acid remains inactive; thus the amount of hydrolyzed acid can be determined according to the increase in sulfuric acid. When, however, on the occasion of the increase of the concentration of sulfur besides the hydrolysis also the sulfonation occurs the chlorobenzenesulfo acid becomes radioactive. Thus the increase of activity of the sulfo acid reflects the increase of the velocity of either process and can be useful for the investi-

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Investigation of the Sulfonation Reaction. XLVII. The SO₂/79-28-6-48/63
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gation of the influence of concentrated sulfuric acid on the
velocity of hydrolysis. There are 2 figures, 1 table, and 6
references, 2 of which are Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut (Ivanovo Chemical
-Technological Institute)

SUBMITTED: May 27, 1957

1. Organic acids--Hydrolysis

Card 3/3

AUTHORS: Spryskov, A. A., Kachurin, O. I. SOV/79-28-8-44/66

TITLE: On the Orientation at Substitution in the Aromatic Series
(*K orientatsii pri zameshchenii v aromaticheskom ryadu*)
IV. Sulfonation of Chlorobenzene (IV. Sul'firovaniye
khlorbenzola)

PERIODICAL: Zhurnal obshchey khimii, 1958, Vol. 28, Nr 8, pp. 2213-2217
(USSR)

ABSTRACT: Since the numerous kinds of sulfonation of chlorobenzene gave for 100 years nothing but the p-chlorobenzene sulfonic acid and a bis-(4-chlorophenyl) sulfone, Holleman (Colleman) (Ref 9) considered it an established fact that in all these reactions only the para-isomer was formed. All publications on this subject (Refs 1 - 9) characterize, but do not exhaust the question of the sulfonation of chlorobenzene. Because of some obvious theoretical considerations the authors regarded it as possible to attain by a change of the sulfonation conditions the other isomers of the chlorobenzene sulfonic acid as well. The results of their studies confirmed their assumption: On sulfonation of the chlorobenzene with sulfuric

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On the Orientation at Substitution in the Aromatic
Series IV. Sulfonation of Chlorobenzene

SOV/79-28-8-44/66

anhydride at -12 up to $+3^{\circ}$ for the first time 1,8-5,8% of o-chlorobenzene sulfonic acid were found. At temperatures of $150-238^{\circ}$, m-chlorobenzene sulfonic acid was formed the quantity of which increased up to a certain degree with further increasing temperature. Thus, the sulfonation by means of sulfuric acid at 238° yields within 12-15 hours a mixture of chlorobenzene sulfonic acid containing more than 50% of the meta-isomer. The ortho-isomer is not formed at increased temperature. The change in the ratio of the isomers at higher temperatures thus confines the applicability of the classical orientation rules in the benzene nucleus. This is seen from tables 1 and 2. In order to determine the isomers of the chlorobenzene sulfonic acid after the sulfonation and to be able to separate them, "semi-quantitative" determinations of the solubility of their salts with 18 amines had been performed (Table 3). Details are given in the experimental section. There are 3 tables and 13 references, 5 of which are Soviet.

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On the Orientation at Substitution in the
Aromatic Series. IV. Sulfonation of Chlorobenzene

SOV/79-28-8-44/66

ASSOCIATION: Ivanovski ~~khimiko~~-tekhnologicheskii institut
(~~Ivanovo~~ Chemical and Technological Institute)

SUBMITTED: July 6, 1957

Card 3/3

KLIVYEV, V.N.; DOGADKINA, L.A.; SOLODUSHENKO, S.N.; SPRYSKOV, A.A.

Azo dyes from amino carbanilide, and its substitutes. Zhur. prikl.
khim. 31 no.1:124-129 Ja '58. (MIRA 11:4)

1.Ivanovskiy khimiko-tekhnologicheskii institut.
(Azo dyes) (Carbanilide)

5(3)

AUTHORS:

Spryskov, A. A., Potapova, T. I.

SOV/153-2-1-8/25

TITLE:

A Study of Sulfonation. Reactions (Izucheniye reaktsii sul'firovaniya).

I. Determination of Isomeric Toluene Disulfonic Acids
(I. Opredeleniye izomernykh disul'fokisl'ot toluola)

PERIODICAL:

Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1959, Vol 2, Nr 1, pp 41-45 (USSR)

ABSTRACT:

During the sulfonation of toluene to monosulfonic acids 3-10% of m-toluene sulphonic acid are formed (Ref 2). With further sulfonation 1,2,5- and 1,3,5-disulfonic acid are produced (Refs 3,4). Up till now only 1,2,4-disulfonic acid was isolated by direct sulfonation of toluene (Ref 1). Altogether four isomers may be formed by sulfonation. These are: 1,2,4-; 1,2,5-; 1,2,6- and 1,3,5-disulfonic acids. Their percentage varies according to the conditions of formation. In order to study the quantitative composition of sulphone mixtures, the authors give a description of the properties of some derivatives of the above-mentioned sulfonic acids, and further, the quantitative method of determining isomers devised accordingly. In this connection there are no data available in publications (with few exceptions mentioned in

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A Study of Sulfonation Reactions.

SOV/153-2-1-8/25

I. Determination of Isomeric Toluene Disulfonic Acids.

reference 4). The isomers were prepared in pure state as acid chlorides according to earlier described methods (Ref 4).
A r y l a m i n e S a l t s. This method was chiefly based on the results obtained by semiquantitative determination of the solubility of the salts of eighteen aromatic amines of toluene-sulfonic acids. Table 1 contains the experimental results which permit the evaluation of the solubility in water with an excess of amine chloro hydrate. Further, the authors made a t h e r m a l a n a l y s i s (results given in figure 1). The corresponding melting diagram indicates that chlorides form no double bonds with one another. The system has, however, an eutectic point which corresponds to 74.2% of 1,2,4-toluene disulfonic chloride and occurs at 35°. In conclusion, the authors gave an i n s t r u c t i o n f o r t h e a n a l y s i s o f s u l f o n i c m i x t u r e s . Thus, they devised a method of quantitative determination of the four afore-mentioned isomers of toluene disulfonic acids in their mixture in the presence of sulphuric acid. The maximum error amounted to about 1-1.5% of the sum of disulfonic acids. There are 3 figures, 2 tables, and 6 references, 2 of which are Soviet.

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A Study of Sulfonation Reactions.
I. Determination of Isomeric Toluene Disulfonic Acids.

SOV/153-2-1-8/25

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut; Kafedra
organicheskoy khimii (Ivanovo Institute of Chemical Technology,
Chair of Organic Chemistry)

SUBMITTED: January 23, 1958

Card 3/3

5(3)

SOV/153-2-3-16/29

AUTHORS:

Spryskov, A. A., Golubkin, L. N.

TITLE:

Production of Radioactive Salicylic Acid

PERIODICAL:

Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i
khimicheskaya tekhnologiya, 1959, Vol 2, Nr 3, pp 392-393 (USSR)

ABSTRACT:

In the present paper the method by Kolbe is applied for the production of salicylic acid tagged with C^{14} in the carboxyl group. Sodium phenolate is carbonized with carbon dioxide which was obtained from $BaC^{14}O_3$ by decomposition. An apparatus which may be used for this synthesis is schematically represented in this paper and exactly described. The finely crushed sodium phenolate is first dried at 140° with a carefully dried hydrogen current during 3-4 hours. The radioactive barium carbonate is decomposed by 95% sulphuric acid saturated with carbon dioxide under heating. The precipitated $C^{14}O_2$ acts at 160° on the dried sodium phenolate. Carbonization lasts 5-10 hours. Air is then introduced in the reaction mixture in order to cool it. A small amount of hydrochloric acid is then

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Production of Radioactive Salicylic Acid

SOV/153-2-3-16/29

added for the decomposition of sodium carbonate. Radioactive salicylic acid is extracted by ether and then extracted from the extract with a sodium bicarbonate solution. After recrystallization with active carbon salicylic acid is dissolved in alcohol and the solution is poured into boiling water. Thus a pure product with the melting point 185.5° is obtained. The activity yield is in this process 45-50%. A number of experiments furnished results which were in good agreement. The course of the synthesis is exactly described. There are 1 figure and 3 references, 1 of which is Soviet.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut, Kafedra organicheskoy khimii (Ivanovo Institute of Chemical Technology, Chair of Organic Chemistry)

SUBMITTED: September 30, 1957

Card 2/2

5(3)
AUTHORS: Spryskov, A. A., Yerykalov, Yu. G. SOV/79-29-8-79/81

TITLE: On the Orientation in the Substitution of the Aromatic Series

PERIODICAL: Zhurnal obshchey khimii, 1959, Vol 29, Nr 8,
pp 2798 - 2803 (USSR)

ABSTRACT: The authors carried out earlier (Ref 1) a number of experiments concerning the isomerization of dichlorobenzenes at 120° and 160°. At 160° a state close to the balance between the isomers was reached and the composition of the mixture in the state of equilibrium was found. However, the balanced state could not be achieved at 120°. In the present paper the further attempts at isomerization at 120° are described, the results of the isomerization experiments at 100 and 180° and of the experiments in which hydrogen chloride was introduced into the reaction mixture are discussed. An investigation was made of the isomerization of the o-, m- and p-dichlorobenzenes at 120 and 180° in the presence of aluminum chloride. In order to achieve the equilibrium between the isomers at 120° many more than 1000 hours are needed. The mixture which is in a state of equilibrium contains 12% o-isomer, 33% p-isomer, and 53% m-isomer. At 180° a state close to equilibrium is

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On the Orientation in the Substitution of the
Aromatic Series

SOV/79-29-8-79/81

reached after 20 hours no matter from which isomer one had started. It was found that the isomerization rate decreases at the introduction of hydrogen chloride into the reaction vessel in proportion to the quantity introduced. The removal of small quantities of HCl from the system also reduces the rate of isomerization according to the reaction mechanism previously suggested (Ref 1). From the experimental data the constants of the isomerization rate of dichlorobenzenes at 160° were computed. More on this computation is found on page 2801. The retarding effect of large amounts of hydrogen chloride on the isomerization may be explained according to the scheme given in the experimental part. There are 1 figure, 3 tables and 3 Soviet references.

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut (Ivanovo Chemical-technological Institute)

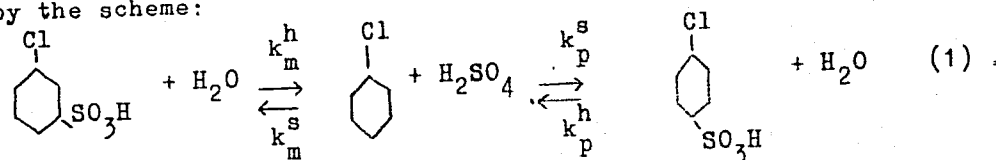
SUBMITTED: June 20, 1958

Card 2/2

S/153/60/003/004/021/040/XX
B020/B054

AUTHORS: Kachurin, O. I., Spryskov, A. A., Mel'nikova, L. P.
TITLE: Study of the Sulfonation Reaction. LIII. Method of Isotopic Exchange for Studying the Kinetics of Hydrolysis of Chloro-benzene Sulfonic Acids
PERIODICAL: Izvestiya vysshikh uchebnykh zavedeniy. Khimiya i khimicheskaya tekhnologiya, 1960, Vol. 3, No. 4, pp. 669 - 674

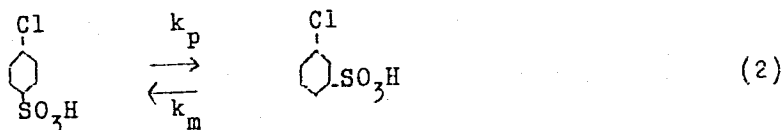
TEXT: The present paper continues the series studying the formation, hydrolysis, and isomerization of chloro-benzene sulfonic acids (Refs. 1,2). In weakly concentrated, aqueous-sulfuric acid solutions, the system investigated can be illustrated with some simplifications by the scheme:



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Study of the Sulfonation Reaction. S/153/60/003/004/021/040/XX
 LIII. Method of Isotopic Exchange for B020/B054
 Studying the Kinetics of Hydrolysis of Chloro-benzene Sulfonic Acids

It appears that two hydrolytic and two sulfonation reactions proceed at the same time, with three organic components participating. On the basis of experimental data, it may be assumed that all reactions in the system proceed at constant water- and sulfuric acid concentrations. Thus, only the previously studied (Ref.2) monomolecular isomerization process



can be determined in the usual manner. To distinguish hydrolysis from a system of four reactions, it is possible to study the isotopic exchange between the sulfonic acids and the sulfuric acid in the solution

Card 2/4

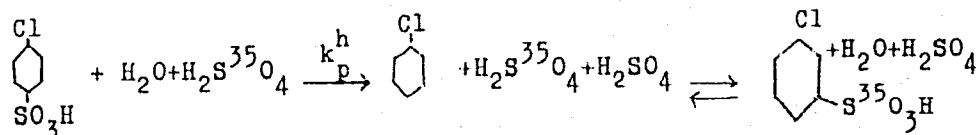
Study of the Sulfonation Reaction.

S/153/60/003/004/021/040/XX

LI. Method of Isotopic Exchange for

B020/B054

Studying the Kinetics of Hydrolysis of Chloro-benzene Sulfonic Acids



The authors observe the exchange of m-chloro-benzene sulfonic acid (Fig.1) and p-chloro-benzene sulfonic acid (Fig.2) with 79.5% of $\text{H}_2\text{S}^{35}\text{O}_4$. The calculated monomolecular constants of the reaction rates are given in Table 1. The logarithms of the mean values for the rate constants are linear to the reciprocal temperatures (Fig.3). Table 2 indicates the values for the activation energies and the logarithms of the exponential functions in the Arrhenius equation. The authors compare the values found for the total rate constants in the isomerization of chloro-benzene sulfonic acids with the calculated values; the isomerization rate was calculated from the equilibrium constant of the isomers and the rate constants of hydrolysis. There are 3 figures, 3 tables, and 4 references: 3 Soviet and 1 British.

Card 3/4

Study of the Sulfonation Reaction. S/153/60/003/004/021/040/XX
LIIL. Method of Isotopic Exchange for B020/B054
Studying the Kinetics of Hydrolysis of Chloro-benzene Sulfonic Acids

ASSOCIATION: Ivanovskiy khimiko-tekhnologicheskii institut, kafedra
organicheskoy khimii (Ivanovo Institute of Chemical
Technology, Department of Organic Chemistry)

SUBMITTED: September 25, 1958

Card 4/4

STARKOV, S.P.; SPRYSKOV, A.A.

Study of the sulfonation reaction. Part No. 52: Formation
of sulfones and their sulfonic acids in the sulfonation of benzene.
Izv. vys. ucheb. zav; khim. i khim. tekhn. 3 no. 5:868-871 '60.
(MIRA 13:12)

1. Ivanovskiy khimiko-tekhnologicheskii institut. Kafedra
organicheskoy khimii.
(Sulfone) (Sulfonic acid) (Benzene)

SPRYSKOV, A.A.

Orientation in substitution in the aromatic series. Part 6:
Orientation of the sulfo group in the sulfonation of toluene.
Zhur.ob.khim. 30 no.8:2449-2453 Ag '60. (MIRA 13:8)

1. Ivanovskiy khimiko-tekhnologicheskii institut.
(Toluene) (Sulfonation)

SPRYSKOV, A.A.

Sulfonation reactions. Part 54: Sulfonation of toluene and isolation of m-toluenesulfonic acid. Izv.vys.ucheb.zav.; khim.i khim.tekh. 4 no.6:981-984 '61. (MIRA 15:3)

1. Ivanovskiy khimiko-tekhnologicheskii institut, kafedra organicheskoy khimii.
(Toluenesulfonic acid) (Toluene) (Sulfonation)

SPRYSKOV, A.A.; YERYKALOV, Yu.G.

Orientation in substitution in the aromatic series. Part 7: Catalysts
of the isomerization of dichlorobenzenes. Zhur. ob. khim. 31 no.1:
292-296 Ja '61. (MIRA 14:1)

1. Ivanovskiy khimiko-tekhnologicheskii institut.
(Benzene) (Izomerization)

SPRYSKOV, A.A.; GOLUBKIN, L.N.

Orientation during substitution in the aromatic series. Part 8:
Effect of the carboxyl group on the reaction of substitution
in the benzene ring. Zhur. ob. khim. 31 no.3:901-905 Mr '61.
(MIRA 14:3)

1. Ivanovskiy khimiko-tekhnologicheskii institut.
(Substitution(Chemistry)) (Carboxyl group)

YERYKALOV, Yu.G.; SPRYSKOV, A.A.

Orientation in the substitution in the aromatic series. Part 9:
Equilibrium between isomers of dichlorobenzene. Zhur. ob. khim.
31 no. 11:3721-3722 N '61. (MIRA 14:11)

1. Ivanovskiy khimiko-tekhnologicheskii institut.
(Benzene) (Substitution (Chemistry))

SPRYSKOV, A.A.; POTAPOVA, T.I.

Reactions of sulfonation. Part 55: Sulfonation of toluene to
disulfonic acids. Izv.vys.ucheb.zav.;khim.i khim.tekh. 5 no.2:
280-283 '62. (MIRA 15:8)

1. Ivanovskiy khimiko-tekhnologicheskii institut, kafedra
organicheskoy khimii.
(Toluene) (Sulfonation)

POTAPOVA, T.I.; SPRYSKOV, A.A.

Reaction of sulfonation. Part 56: Isomerization of
toluenedisulfonic acids. Izv.vys.uch.zav.; ~~khim.i.khim.~~
tekh. 5 no.4:594-600 '62. (MIRA 15:12)

1. Ivanovskiy khimiko-tehnologicheskii institut, kafedra
organicheskoy khimii.
(Toluenedisulfonic acid)
(Isomerization)

YERYKALOV, Yu. G.; SPRYSKOV, A. A.

Preparation of meta-dichlorobenzene and 2,4-dichloronitrobenzene. Izv. vys. ucheb. zav.; khim. i khim. tekhn. 5 no.5: 763-765 '62. (MIRA 16:1)

1. Ivanovskiy khimiko-tekhnologicheskii institut, kafedra organicheskoy khimii.

(Benzene)

YERYKALOV, Yu. G.; SPRYSKOV, A. A.; YEFIMOVA, E. M.

Orientation during substitution in the aromatic series.

Part 11: Isomerization of trichlorobenzenes. Zhur. ob. khim.

32 no.12:4025-4028 -D '62.

(MIRA 16:1)

1. Ivanovskiy khimiko-tekhnologicheskoy institut.

(Benzene) (Isomerization)

KACHURIN, O.I.; SPRYSKOV, A.A.; KOVALENKO, E.V.

Sulfuration reaction. Part 57: Kinetics of sulfonation of benzene in nitrobenzene. Izv. vys. ucheb. zav.; khim. i khim. tekhn. 6 no.3:425-433 '63. (MIRA 16:8)

1. Ivanovskiy khimiko-tekhnologicheskii institut, kafedra organicheskoy khimii.
(Sulfonation) (Benzene)

SPRYSKOV, A.A.; GNEDIN, B.G.

Orientation in the substitution in the aromatic series. Part 10:
Sulfuration of toluene at low temperatures. Zhur.ob.khim. 33 no.4:
1082-1085 Ap '63. (MIRA 16:5)
(Toluene) (Sulfuration)

SPRYSKOV, A.A.; BARVINSKAYA, I.K.; KARAVAYEV, B.I.

Orientation during substitution in the aromatic series. Part 12:
Orientation of a nitro group during low temperature nitration of
nitrobenzene. Zhur.ob.khim. 33 no.6:1885-1893 Je '63.
(MIRA 16:7)

1. Ivanovskiy khimiko-tekhnologicheskii institut.
(Nitrobenzene) (Nitration)